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The Separation of the Sub-Group Arsenic, Antimony and Tin from the Sulphide Group of Elements

Chemical Engineering

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THE SEPARATION OF THE SUB-GROUP ARSENIC, ANTIMONY AND TIN FROM THE SULPHIDE GROUP OF ELEMENTS

BY

LEO A. MAUTNER

THESIS FOR THE DEGREE OF BACHELOR OF SCIENCE

IN CHEMICAL ENGINEERING

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Leo A. Mautner

ENTITLED The Separation of the Sub-Group Arsenic, Antimony, and Tin from the Sulphide Group of Elements.

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

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S. W. Parr
Instructor in Charge

APPROVED: W. A. Noyes

HEAD OF DEPARTMENT OF Chemistry

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The science and art of making alloys dates back to the days of ancient history. The Greeks and Romans made bronzes and amalgams but they had only a few metals for compounding, such as tin, gold, copper, iron, silver and mercury. As the other metals came into use, more combinations were possible until today there are almost numberless alloys having different constitution and properties. The effects of varying amounts of certain metals were studied and at the present time we know what properties certain metals have and what properties they will give to alloys in which they are used. Some increase or decrease the specific gravity, others the hardness, others the ductility, others the conductivity, others the resistance to corrosion by weathering and acids, etc.

There is a very important group of alloys such as brasses, bronzes,* gun metals, bell metals, babbitts, type metals, solders, Brittania metal, etc. These contain chiefly copper, lead, tin and antimony, with some other metals such as nickel, iron, cobalt, aluminum, and zinc. A variation, in small amounts of any of these metals may produce a large change in the property of the alloy so that it becomes important to have an accurate analysis of the alloy in question. It is expedient therefore, to have a method of analysis which is accurate, speedy and simple for use in industrial laboratories where a knowledge of the exact composition is essential.

We shall consider the separation of those metals, which are most common and most important in the alloys mentioned above,

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*Brass is essentially an alloy of copper and zinc and usually lead. Bronzes are composed mainly of copper and tin and lead.

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e.g. antimony, tin, copper, lead, bismuth, and cadmium. There are many separations which depend upon the solubility of antimony and tin sulphides in yellow ammonium sulphide, thus separating them from the sulphides of copper, lead, bismuth and cadmium.

This method is unsatisfactory in that it requires several hours standing for complete dissolving of the antimony and tin sulphides; large amounts of free sulphur are introduced which are annoying; and, the fact that yellow ammonium sulphide also dissolves copper and bismuth sulphides, to a certain extent, makes it undesirable. There are many methods described in literature for the separation of arsenic, antimony and tin, and the separation of mercury, lead, copper, bismuth and cadmium. The following will be a rapid review of the most important processes.

Drown's[1] method depends upon the volatilization of the chlorides of arsenic, antimony and tin, which are absorbed in potassium bromide. The arsenic is distilled from this and the antimony and tin are separated by Garnot's method. Separations based upon the volatilization of certain metals are not looked upon with much favor in commercial laboratories because of their unreliability, expensive and delicate apparatus necessary and the length of time required for an analysis.

Garnot's[2] method adds an excess of oxalic acid to a neutral hydrochloric acid solution of tin and antimony. When this is treated with sodium thiosulphate, the antimony is precipitated as the sulphide, but the tin is held in solution by the oxalic acid. The difficulty here lies in the fact that very often the tin also precipitates with the antimony.

Bunsen[3] uses a 5% solution of potassium hydroxide to separate the sulphides of arsenic and antimony from those of copper, lead, etc., giving arsenates and antimonates. The arsenic is then volatilized by means of chlorine gas. This method works satisfactorily when tin is not present as we shall see later. The difficulties here lie in the fact that most alloys will contain tin with antimony and the same objections to volatilization methods in technical laboratories as were previously stated.

Warren's[4] method directs the dissolving of the sulphides of antimony and tin in the presence of copper, lead etc. sulphides, with sodium hydroxide. The filtrate is treated with hydrochloric acid thus precipitating the sulphides of antimony and tin. These are filtered and dissolved in aqua regia. Potassium ferrocyanide is added to the latter solution and the tin precipitated as stannic ferrocyanide. The antimony remains in solution, antimonic ferrocyanide being unknown. In this method the same difficulty, which will be taken up later, is encountered.

Dinam[5] suggests a method for the separation of arsenic, antimony and tin which can be directly applied to the analysis of alloys. The alloy is treated with nitric acid which dissolves all the metals except arsenic, antimony and tin. The latter are then dissolved with oxalic acid, ammonium oxalate and a little hydrochloric acid. Hydrogen sulphide gas is passed into this solution thus precipitating the sulphides of arsenic and antimony. The tin is determined electrolytically from the filtrate. The arsenic and antimony sulphides are dissolved in potassium hydroxide, a little hydrochloric acid is added and the hydrogen sulphide expelled by

boiling. The arsenic is precipitated as the sulphide, while the antimony remains in solution. The antimony is oxidized with hydrochloric acid and potassium chlorate and the chlorine expelled by boiling. This is then treated with potassium iodide and the liberated iodine titrated with sodium thiosulphate. The arsenic sulphide is dissolved in potassium hydroxide, oxidized as in case of antimony, treated with potassium iodide and the liberated iodine titrated with sodium thiosulphate. The first question here is as to the insolubility of arsenic and antimony in nitric acid. Another difficulty is the unreliability due to the fact that all chlorine must be expelled before addition of potassium iodide, and is so much boiling and evaporating down as this necessitates, considerable error may result in volatilization of arsenic and antimony.

Berg's[6] method can be directly applied to the analysis of alloys. He heats the finely divided alloy with sodium carbonate and sulphur in a porcelain crucible. The tin is changed to sodium sulpho-stannate and the antimony goes over into antimony trisulphide. This mass is placed in water where the sodium sulpho-stannate is dissolved while the antimony trisulphide remains in the residue.

Marburg[7] proposes a method of separation of arsenic, antimony and tin sulphides based upon the fact that arsenic and antimony sulphides are soluble in lime water while tin sulphide is insoluble.

Lang, Carson, and Mackintosh[8] devised a method wherein the sulphide of arsenic, antimony and tin are treated with concentrated nitric acid and brought to dryness. The residue is extracted with water and the arsenic is dissolved and determined with magnesia

mixture. The residue is digested with tartaric acid which extracts the antimony. These operations, such as evaporating to dryness, etc. are undesirable on account of the tedious nature of the operations and the question as to the sharpness of the separation.

Weller's[9] method for the separation of antimony and tin is based on the fact that an acid solution of antimonic chloride and stannic chloride, only the antimony is reduced by potassium iodide.

Herronn[10] describes a method for the volumetric determination of antimony in the presence of tin. The antimony tetrachloride is reduced to the dichloride by hydrochloric acid in the presence of tin tetrachloride.

Causse[11] suggests another volumetric method for the determination of antimony. Antimonic acid, either free or combined, is destroyed when it comes in contact with iodic acid, and the amount of iodine set free is proportional to the amount of iodic acid decomposed:

$$5Sb_2O_3 + 2IO_5 = Sb_2O_5 + 2I_2$$

Clarke's[12] method consists in treating a hydrochloric acid solution of arsenic, antimony and tin with oxalic acid. When hydrogen sulphide is passed into this solution the arsenic and antimony are precipitated as sulphides while the tin is kept in solution by the oxalic acid. The arsenic and antimony sulphide are filtered off and the tin precipitated from the filtrate with excess of acetic acid.

D. J. Demorest[13] gives the following method for analysis of babbitt metals, solders and journal brasses. After the alloy is

dissolved in nitric and tartaric acids, the lead and copper are precipitated by sodium sulphide, the lead and copper sulphide redissolved in nitric acid and again precipitated to recover small amounts of antimony and tin. These sulphides of lead and copper are again dissolved in nitric acid and determined electrolytically. The sulphides of antimony and tin are dissolved in yellow ammonium sulphide and the antimony and tin deposited on a platinum cathode electrolytically. After weighing the deposit the metals are dissolved off the cathode and the antimony determined by iodimetry.

C. E. Swett[14] gives a method for determining bismuth in alloys containing lead and tin. The acid filtrate of mixed nitrates, filtered from stannic oxide, is treated with excess of potassium or sodium hydroxide. This precipitates the bismuth and cadmium, and the lead hydroxide is redissolved. The oxides of bismuth and cadmium are dissolved in hydrochloric acid and bismuth precipitated by diluting the filtrate.

A. J. Hall and C. W. Dillon[15] propose a method for determination of aluminium in brasses and bronzes. Since this metal is often present in these alloys a mention of this method here should not be amiss. The alloy is dissolved in aqua regia, evaporated to dryness, taken up with hydrochloric acid and diluted. Hydrogen sulphide is passed through the solution and the sulphides filtered off. The filtrate is oxidized and the aluminium precipitated as a phosphate.

The foregoing is a rapid review of the most important methods of separating arsenic, antimony and tin. In spite of the fact that this separation has received much attention, there is no

fast, accurate method which is entirely reliable. It was not our intention to devise a new method for the separation of arsenic, antimony and tin from each other, or their separation from copper, lead, bismuth and cadmium; but to try if possible to find the best method for the former and to improve the latter.

The fact that the sulphides of arsenic, antimony and tin are soluble in fixed alkali, while those of copper, lead, bismuth and cadmium are not, has been known for many years but has not been used successfully in this separation. It is to be noted in the review of the literature that this fact is recognized in a general way by ~~Br~~Bunsen[3] and Dinam[5] who make use of it for dissolving out the sulphides of arsenic and antimony. From the fact that they restrict its use to these elements we must infer that they found it inapplicable to tin sulphides. On the contrary Warren[4] bases his separation on the solubility of the sulphides of both tin and antimony in sodium hydroxide. That a difficulty resides in the use of sodium and potassium hydroxide is evident and the study of the process has been the chief element in the experimental work taken up later. Therefore it was our purpose to try, if possible, to find an explanation which also might lead to the use of the fixed alkali hydroxide as a method of separating these sulphides.

EXPERIMENTAL WORK

The first step in the analysis of alloys is the dissolving of the same. There were different brasses, bronzes, bearings, and babbitts at hand and used for this part of the work. It was found that all these would dissolve by the following method:

Concentrated hydrochloric acid was added to the sample and heated to boiling on a hot place. Concentrated nitric acid was added, small quantities at a time, until all of the alloy was dissolved. The nitric acid was then driven off by heating and addition of some more hydrochloric acid. When the brown fumes ceased to come off the solution was diluted with water which contained some potassium tartrate. The potassium tartrate kept the antimony oxychloride from precipitating. Although the sulphide of antimony can be obtained by use of hydrogen sulphide in the presence of the oxychloride, it is difficult to effect a complete transformation and there is no way to tell when the change to the sulphide has been completed.

The next thing considered was the best method of precipitating the metals as sulphides. Hydrogen sulphide gas has been most popular and efficient but is annoying on account of its disagreeable odor and its poisonous nature. Walter Burrows Brown[16] has suggested the use of thio-acetic acid as a substitute for hydrogen sulphide. This was tried but not found very satisfactory because it took too much of the reagent, which is expensive, and liberated large quantities of free sulphur. It was decided that in spite of the above mentioned objections, hydrogen sulphide was the best precipitating medium at hand.

Standard solutions of arsenic, antimony, tin, copper, lead, bismuth and cadmium were made up from the purest metals obtainable. They were dissolved according to the method previously described. These included both trivalent and pentavalent arsenic and antimony, and stannous and stannic tin. The sulphides of these metals were to

be precipitated by means of hydrogen sulphide gas. In the use of the latter the two things to be considered are: (1) complete precipitation of the metals, and, (2) the absence of the colloidal condition. To procure these conditions the following method of precipitation was adopted. The hydrogen sulphide is passed through the solution in the cold for fifteen minutes. It is then put on the hot water bath and the gas passed for twenty minutes more. At the close of these twenty minutes the solution should practically have reached the boiling point. The sulphides are filtered while hot and if the solution becomes cold it was found advisable to warm it in order to hasten the filtering and to procure a clear filtrate. This proceedure was found to completely precipitate all the metals and to give no trouble in filtering.

Sulphides were precipitated by this method from solutions containing one of the metals such as arsenic, antimony, tin, lead, copper, bismuth or cadmium. These sulphides were treated with solutions of potassium hydroxide of varying concentrations of from 1/2% to 5%:

PbS	+	1/2%	KOH	+ boiling =	no	trace	of	PbS	dissolved
"	"	1%	"	"	"	"	"	"	"
"	"	2%	"	"	"	"	"	"	"
"	"	3%	"	"	"	"	"	"	"
"	"	5%	"	"	"	"	"	"	"

Bi_2S_3	+	1/2%	KOH	+ boiling =	no	trace	of	Bi_2S_3	dissolved
"	"	1%	"	"	"	"	"	"	"
"	"	2%	"	"	"	"	"	"	"
"	"	3%	"	"	"	"	"	"	"
"	"	5%	"	"	"	"	"	"	"

CuS + 1/2% KOH + boiling = no trace of CuS dissolved

" " 1% " " " " " " " "

" " 2% " " " " " " " "

" " 3% " " " " " " " "

" " 4% " " " " " " " "

CdS + 1/2% KOH + boiling = no trace of CdS dissolved

" " 1% " " " " " " "

" " 2% " " " " " " "

" " 3% " " " " " " "

" " 5% " " " " " " "

As_2S_3 + 1/2% KOH + boiling = complete solution without repptn.

" " 1% " " " " " " "

" " 2% " " " " " " "

" " 3% " " " " " " "

" " 5% " " " " " " "

$2AS_2S_3 + 4KOH = KASO_2 + 3KAsS_2 + 2H_2O$

As_2S_5 + 1/2% KOH + boiling = complete solution without repptn.

" " 1% " " " " " "

" " 2% " " " " " "

" " 3% " " " " " "

" " 5% " " " " " "

$3As_2S_5 + 6KOH = KAsO_3 + 5KAsS_3 + 3H_2O$

Sb_2S_3 + 1/2% KOH + boiling = complete solution without repptn.

" " 1% " " " " " "

" " 2% " " " " " "

" " 3% " " " " " "

Sb_2S_3 + 5% KOH + boiling = complete solution without repptn.

$4Sb_2S_3 + 8KOH = 6KSbS_2 + 2KSbO_2 + 4H_2O$

Sb_2S_5 + 1/2% KOH + boiling = complete solution without repptn.

" " 1% " " " " " "

" " 2% " " " " " "

" " 3% " " " " " "

" " 5% " " " " " "

$3Sb_2S_5 + 6KOH = 5KSbS_3 + KSbO_3 + 3H_2O$

SnS +1/2% KOH + boiling = difficulty soluble

" " 1% " " " "

" " 2% " " " "

" " 3% " " " "

" " 5% " " = solution with slight turbidity.

$2SnS + 4KOH = K_2SnO_2 + K_2SnS_2 + 2H_2O$ (?)

This is the probable reaction.

SnS_2 + 1/2% KOH + boiling = complete solution with repptn.

" " 1% " " " " " "

" " 2% " " " " " "

" " 3% " " " " " "

" " 5% " " " " " "

The probable equation for the dissolving of SnS_2 by KOH is

$3SnS_2 + 6KOH = K_2SnO_3 + 2K_2SnS_3 + 3H_2O$

Thus it can be seen that for complete solution of the sulphide of arsenic, antimony and tin the conditions must be found under which the tin will not reprecipitate after it has been

dissolved as the sulphide. The fact that Bunsen and Dinarn confine the use of potassium hydroxide to antimony and arsenic sulphides shows that they must have encountered difficulties or seen good reasons for not including tin sulphide as being subject to the same action. This is shown by the work of Hagedorn,[17] Kutsch,[18] Steinwedell[19] and the others who have studied this problem in this laboratory. In contrast to this, Warren includes tin in the use of potassium hydroxide, and Hagedorn and Turnock[20] seemed to have found conditions under which tin sulphide will dissolve as easily as the others and not cause any reprecipitation of the tin. This variation and contradiction of results has led us to believe that under certain specific conditions, the tin will act normally, and it is our purpose to discover these conditions and present them in such a manner that there shall be no exceptions. This of course can only be done by gaining an understanding of the principles involved. The fact that under certain conditions the tin will reprecipitate and under others it will remain indefinitely in solution must therefore be modified with respect to this state of uncertainty if we are to safely use it in analysis.

The effect of free sulphur was first investigated. The free sulphur may react with potassium hydroxide to form potassium thiosulphate:

$$6KOH + 4S = 2K_2S + K_2S_2O_3 + 3H_2O$$

Some potassium thiosulphate was added to an alkaline solution of tin and a white precipitate was formed. This shows that under the conditions with which we are working the tin will be precipitated by potassium thiosulphate, so that the reprecipitation

of tin may be due to the formation of this hyposulphite. A solution containing .2 gram of tin was made very slightly acid so that very little free sulphur would be thrown down by passing hydrogen sulphide into the solution. The precipitate dissolved in a 4% solution of potassium hydroxide, but there was a reprecipitation. Another solution of tin was made decidedly acid so that considerable sulphur would be present. The precipitate from this solution also dissolved in potassium hydroxide after which the usual reprecipitation of tin occurred. A third sample was made acid and some hydrogen peroxide added so that a large excess of free sulphur would be liberated. This precipitate acted the same as the previous two. From these results we can see that the tin sulphide will always dissolve in presence of various amounts of sulphur and that the tin hydrate precipitates whether there is a minimum amount of free sulphur present or an excess.

The fact that temperature might have some effect, caused us to consider that feature. Solutions of potassium hydroxide of varying strengths from 1/2% to 5% were made up. Hot alkali solutions were added to the tin sulphide in the cold; hot potassium hydroxide solutions were added to the hot sulphide; cold alkali hydroxide solutions were added to hot sulphides and then to cold sulphides. In all these cases there was a reprecipitation.

In running blanks with these experiments it was found best to use freshly prepared solutions of potassium hydroxide and to carry out the dissolving of the sulphides in casseroles. Alkali hydroxides upon standing in glass bottles, or boiling in glass beakers may dissolve out some aluminum or silica which may be later thrown

down as a white gelatinous precipitate which resembles the tin hydroxide. Another reason for using freshly prepared potassium hydroxide is that upon standing it will absorb carbon dioxide, forming alkali carbonates which will precipitate the tin. The tin solution should also be freshly prepared. We noticed that, upon long standing, the standard solutions of tin became turbid. This is due to the formation of metastannic chloride. If the sulphide is precipitated from this, and then dissolved in potassium hydroxide, there will be a residue of potassium metastannate.[21]

In dissolving the tin sulphide in alkali hydroxide, it was noticed that sometimes there was a change in the color of the solution before the sulphide dissolved. If the alkali hydroxide is added slowly this color, which varies from yellow to deep red, always appears. This color, however, disappears upon boiling or addition of more alkali hydroxide. This may be due to the formation of potassium sulphide which is decomposed upon boiling, liberating free sulphur, which might react with the hot potassium hydroxide to form the potassium thiosulphate:

$$6KOH + 4S = 2K_2S + K_2S_2O_3 + 3H_2O$$

Since hydrogen peroxide will oxidize any possible potassium thiosulphate to potassium sulphate, the addition of a little of the peroxide was tried. It was found best to mix the peroxide with the potassium hydroxide before adding the same to the sulphide.

This mixture of alkali hydroxide and hydrogen peroxide was added until the sulphide was all dissolved. In the majority of the

cases the tin sulphide went into solution easily without reprecipitation, but occassionally there would be an exception and the same difficulty due to reprecipitation would arise. It was evident that there were some conditions which controlled this behavior.

The amount of potassium hydroxide to use for complete solution of the sulphides, with reference to amount necessary to make the solution alkaline was investigated. By bringing the material just past the neutral point, very often a dark colored solution would result, and upon boiling the precipitate turned dark brown. If a few drops of potassium hydroxide were then added the precipitate immediately dissolved and the solution turned colorless. Upon adding an excess of potassium hydroxide, to this, and boiling, the tin hydrate would precipitate. The operation was then carried out without addition of the excess of potassium hydroxide and without boiling after being brought just past the neutral point. This gave a clear solution which upon standing as long as seventy-two hours gave no reprecipitate. These results were absolutely consistent and not one exception was found, In each case a solution of 100 c.c. of 5% potassium hydroxide plus 1 c.c. of 30% hydrogen peroxide was freshly prepared for use.

Although no definite conclusions have been reached as to what the exact chemical reactions are during this process, still a few hypothetical explanations are suggested as being sufficiently plausible for a working basis. The fact that potassium thiosulphate may be the precipitating medium of the tin hydrate, and the use of hydrogen peroxide to prevent its formation, has been discussed. This explanation suffers a contradiction, however, because of the

fact that several times a complete solution of the sulphides has been obtained, without the slightest reprecipitation of the tin, where the use of hydrogen peroxide has been avoided. This can be explained by the following; either there is an absence of free sulphur in the stannic sulphide, thus eliminating the possibility of the formation of potassium thiosulphate, or, if just enough potassium hydroxide is added after the neutral point has been reached, it will all be used in forming the oxy and sulpho salts of tin, but if a small excess is added this will react with the free sulphur and form the hyposulphite which will precipitate the tin hydroxide. If, however, the hydrogen peroxide is present to oxidize any hyposulphite which may be formed in this manner, the tin will not be subject to the action of that reagent. As it is impossible to tell exactly how much potassium hydroxide is necessary, it is not safe to omit the use of the hydrogen peroxide. As has been previously stated, the tin often goes over into the metastannate form, and it may be that the hydrate of tin is precipitated from an alkaline solution of metastannate tin. This latter statement seems to receive confirmation from the fact that an excess of hydrogen peroxide does precipitate the tin. The theory being that an excess of hydrogen peroxide changes the tin into the metastannate form, in which form it is insoluble in potassium hydroxide. Only enough hydrogen peroxide therefore should be added to care for the oxidation of the soluble sulphur compounds.

The action of this method upon the sulphides of antimony, arsenic, lead, copper, bismuth and cadmium was investigated. The trivalent and pentavalent sulphides of arsenic and antimony went

into solution easily without any reprecipitation. The sulphides of lead, copper, bismuth and cadmium were not at all dissolved. One would suspect that, in the presence of hydrogen peroxide, the copper sulphide would be oxidized to the sulphate and dissolve. This is not possible in this separation because there is so very little hydrogen peroxide present, and if any copper should be dissolved it would be reprecipitated as the oxide by the potassium hydroxide.

The method, therefore, developed for the separation of the sub-group arsenic, antimony and tin, from the sulphide group of elements, is as follows:

Filter the sulphides and wash them with slightly acid hydrogen sulphide waters. Wash them into a porcelain casserole with this same water and heat to boiling. Add slowly, continually boiling and stirring, potassium hydroxide and hydrogen peroxide, from a solution made up as follows: 100 c.c. 5% potassium hydroxide plus 1 c.c. 30% hydrogen peroxide. When the solution is just past neutral, boil it for two or three minutes and after removing the flame add three or four c.c. more of the solvent and allow the solution to stand for a few minutes. This will completely dissolve all the arsenic, antimony, and tin, and leave the copper, bismuth, lead, and cadmium in the precipitate form. These are filtered and washed. The filtrate contains the arsenic, antimony and tin, which can be separated by any standard method.

The entire process of separating these groups of sulphides does not require more than fifteen or twenty minutes, is simple and accurate.

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